the structure. Although the geometrical isomers are not bound to be of identical energy, the refinement of the occupancy factors of C(17), C(20), and C(21) (see above) showed that both isomers are equally distributed throughout the crystal.

Bond lengths and angles in the ligand molecule (Table V) are in agreement within their standard deviations with values from other salicylaldimine complexes.[27] It appears however that standard deviations on distances and angles including atoms involved in the disorder are somewhat optimistic. The equations of some significant least-squares planes and the deviations of the atoms from these planes are reported in Table VI. It can be noted that the nickel atom is not symmetrically displaced from the salicylaldimine planes, the two distances being 0.37 and 0.78 Å. The angle between the two planes passing through the salicylaldimine moieties is 101.0°.

Inspection of the intermolecular distances below 3.6 Å shows that there are no unusually short contacts between molecules (Table VII).

TABLE VII
INTERMOLECULAR CONTACTS BELOW 3.6 Å

Atom 1	Atom 2	Dist, Å
C(3)	C(15) $(x + 1, y, z)$	3.35
C(18)	O(2) $(x + 1, y, z)$	3.57
C(18)	C(10) $(x + 1, y, z)$	3.50
C(13)	C(20)′ $(\bar{x}, \bar{y}, \bar{z} + 1)$	3.46
C(10)	C(21)′ $(\bar{x}, y + {}^1/_2, \bar{z} + {}^1/_2)$	3.57

Finally it should be mentioned that this structure represents an unusual case of a pentacoordinated complex formed by a pentadentate ligand. Only recently another similar case has been reported,[26] in which the pentadentate ligand tpen (*N,N,N′*-tris(2-(2′-pyridyl)-ethyl)ethylenediamine) forms a square-pyramidal stereochemistry around the nickel atom.

[27] E. C. Lingafelter and R. L. Braun, *J. Amer. Chem. Soc.*, **88**, 2951 (1966).

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The Crystal Structure, Absolute Configuration, and Circular Dichroism of a Cobalt(III) Complex of an Optically Active Triethylenetetramine Homolog, $(+)_{589}$-*trans*-($(-)_{589}$-*N,N′*-Bis((*S*)-2-amino-3-phenylpropyl)-*trans*-(*R*)-1,2-cyclohexanediamine-δλδ)dichlorocobalt(III) Perchlorate

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This complex $[Co(C_{24}H_{36}N_4)Cl_2]ClO_4$ crystallizes in space group $P2_1$ with unit cell dimensions of $a = 13.237 \pm 0.007$ Å, $b = 16.671 \pm 0.009$ Å, $c = 12.988 \pm 0.006$ Å, $\beta = 94.81 \pm 0.02°$, $Z = 4$, and $\rho_{calcd} = 1.416 \pm 0.003$ g cm^{-3} at 23°. The structure was solved by the heavy-atom method with 2277 observed reflections collected on an automatic diffractometer. Refinement proceeded anisotropically for Co and Cl and isotropically for the remaining light atoms to a final reliability index $R_1 = 0.096$. The Cl atoms show trans coordination, and the absolute configuration has been verified from anomalous dispersion data. Both molecules in the asymmetric unit have the same conformation in the coordination sphere, but pendant groups show differences in orientation caused by crystal packing requirements. Average bond lengths in the coordination octahedra are Co–N = 1.96 ± 0.01 Å and Co–Cl = 2.260 ± 0.008 Å. Optical rotatory dispersion, circular dichroism, and absorption spectra for this complex are shown and compared with spectra for similar complexes in the literature. The correlation of these spectra with absolute configuration and the conformation of the chelate rings is discussed.

Introduction

The assignment of absolute configuration and chelate ring conformation on the basis of optical rotatory dispersion (ORD) and circular dichroism (CD) data has too often been incorrect. Robinson, *et al.*, pointed out the need for care in making such assignments "even for complexes which have similar visible absorption spectra and chromophores which have effectively D_{4h} symmetry."[1] Reference molecules are needed for which both crystal and molecular structure and the circular dichroism data are known in detail. Preferably, these should have high conformational and configurational stability to minimize the possibility of alteration during phase changes from solution to solid. Recently a new tetradentate ligand with four optical centers of different relative configurations has been reported.[2] In a Co(III) complex, the ligand is strongly stereoselective for the trans isomer (Figure 1), and the only other isomer observed, the L-cis-β, readily isomerizes to the trans geometry. Initially, a D-cis-α isomer was predicted by analogy with (*S,S*)-α,α′-$(CH_3)_2$trien which complexes with Co(III) to give 95% D-cis-α, 4% L-cis-β, and 1% trans isomers.[3] As in the new ligand, the backbone of this trien molecule has a configuration

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[1] W. T. Robinson, D. A. Buckingham, G. Chandler, L. G. Marzilli, and A. M. Sargeson, *Chem. Commun.*, 539 (1969).

[2] R. G. Asperger, *Inorg. Chem.*, **8**, 2127 (1969).

[3] R. G. Asperger and C. F. Liu, *ibid.*, **4**, 1395 (1965).

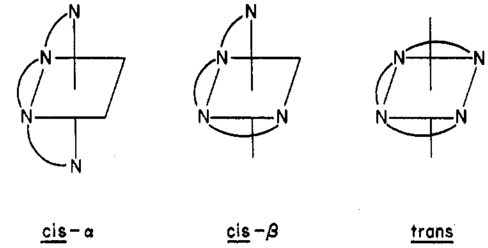

Figure 1.—Geometric isomers in an octahedral complex. Cis forms occur as enantiomeric pairs giving a total of five possible isomers.

opposite to that in the two arms, both of which have the same configuration. We report here a single-crystal X-ray diffraction study of the perchlorate salt of a Co(III) ion complex of the new ligand *N,N'*-bis((*S*)-2-amino-3-phenylpropyl)-*trans*-(*R*)-1,2-cyclohexanediamine and the correlation of the ORD and CD spectra with the established structure. The work was undertaken to provide a reference of the type discussed above.

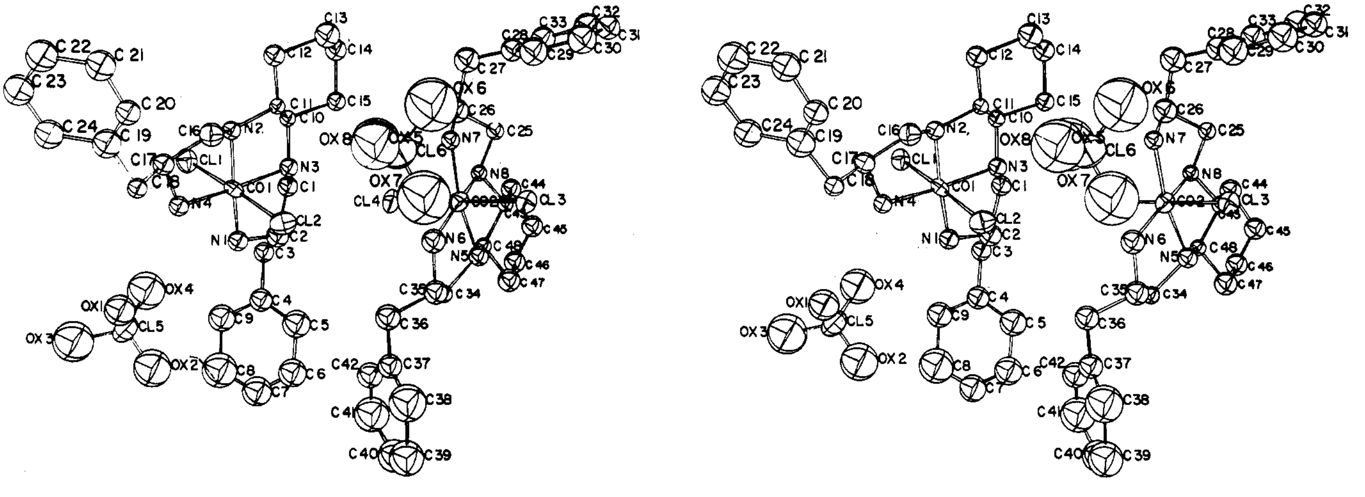

Figure 2.—Stereoview of $[Co(C_{24}H_{36}N_4)Cl_2]ClO_4$.

Experimental Section

X-Ray Data and Solution of Structure.—All procedures were carried out at prevailing room temperatues of approximately 23°. The complex $Co[C_{24}Cl_2H_{36}N_4]ClO_4$ (I) forms bright green crystals in the shape of elongated prisms. Weissenberg photographs show monoclinic diffraction symmetry C_{2h} and systematic absences for $0k0$ with k odd, characteristic for space groups $P2_1$ and $P2_1/m$, but only $P2_1$ is consistent with the optical activity of the complex. A crystal of dimensions 0.06 × 0.10 × 0.30 mm, perpendicular to faces (001), (100), and (010), respectively, was mounted on a card-controlled Picker four-circle diffractometer with the *b* axis parallel with ϕ. Using Cu Kα radiation (λ 1.5418 Å), unit cell dimensions of $a = 13.237 \pm 0.007$ Å, $b = 16.671 \pm 0.009$ Å, $c = 12.988 \pm 0.006$ Å, and $\beta = 94.81 \pm 0.02°$ were obtained from a least-squares fit of the setting angles for 12 reflections; a factor of 3 was applied to the estimated standard deviations from the least-squares calculation to give the reported values. Four formula units per unit cell give a reasonable calculated density of 1.416 g cm^{-3} and the structure study thereby required the determination of parameters for 72 independent atoms.

Intensities for 5567 *hkl* reflections and 5142 $\bar{h}\bar{k}\bar{l}$ reflections were measured on the automatic diffractometer using Cu Kα radiation with the 100 reflection of a highly oriented graphite crystal monochromator.[4] Settings were based on a reference set of 12 reflections measured manually. The takeoff angle for the X-ray tube was 4°, the scintillation detector with a 4.0-mm square aperture was placed 26 cm from the crystal, and the pulse-height analyzer was optimized for the radiation in conjunction with the graphite monochromator. Data were collected in the 2θ scan mode with a 1°/min scan rate over a scan range which varied from 2.1 to 5.2° in going to the maximum sin θ value of 0.909. Background counts of 20 sec were taken at each end of a scan using the stationary-crystal, stationary-counter technique. Corrections for Lorentz and polarization effects were made, and an error $\sigma(I) = [(0.03I)^2 + N_0 + k^2N_b]^{1/2}$ was assigned to the net intensities $I = N_0 - kN_b$ and used to calculate the weights $w = 4F^2/\sigma^2(F^2)$ for the least-squares structure refinement minimizing $\Sigma(wF_o - F_c)^2$. Here N_0 is the gross count, N_b is the background count, and k is the ratio of scan time to background time. Using the arbitrary criterion $I \geqslant 3\sigma(I)$ to distinguish observed from nonobserved intensities resulted in final data sets of 2277 *hkl* reflections and 2303 $\bar{h}\bar{k}\bar{l}$ reflections. The linear absorption coefficient is 74.93 cm^{-1}, and a general absorption correction was made[5,6] giving transmission coefficients ranging from 0.39 to 0.66. A Wilson plot was used to obtain initial scale and overall temperature factors.

Seven of the eight heavy atoms in the asymmetric unit were found in a Patterson map and used for initial phasing of electron density maps from which all remaining atoms (65) were found in two cycles. After isotropic refinement to reliability indices $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.148$ and $R_2 = \{\Sigma w(F_o - F_c)^2/\Sigma wF_o^2\}^{1/2} = 0.166$, values of $\Delta f'$ and $\Delta f''$ for Co and Cl were introduced and calculations were done for each of the two possible mirror image structures.[7] R_1, R_2 values of 0.130, 0.135 and 0.133, 0.141 were judged to be different enough for these calculations to identify the correct enantiomer, and refinement proceeded anisotropically for Co and Cl and isotropically for the remaining

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(4) T. C. Furnas, Jr., and D. W. Beard, Paper E3, American Crystallographic Association Meeting, Minneapolis, Minn., Aug 22, 1967.

(5) J. DeMeulenaer and H. Tompa, *Acta Crystallogr.*, **19**, 1014 (1965).

(6) Local programs used with the IBM 1130 computer include DIFCL and DIFST for automatic diffractometer setup, XRDP5 for data reduction, WILPT for a Wilson plot, PASHCO to produce sharpened Patterson coefficients, LSQPL to fit planes and lines by the method of Shoemaker *et al.*, and JOURN to prepare F_o, F_c tables. In addition, a version of C. K. Johnson's ORTEP thermal ellipsoid plotting program, adapted to the IBM 1130 by T. P. Blumer, was used. A CDC 3800 was used for D'Addario and Knox's version of Byungkook-Lee's absorption program ABSCORR, for Gvildy's versions of Busing, Martin, and Levy's ORFLS and ORFFE least-squares and function and error programs, and for his version of Sly and Shoemaker's MIFRI Fourier summation program.

(7) Atomic scattering factors for neutral atoms are from J. A. Ibers, "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, Engand, 1962, Table 3.3.1A, and dispersion corrections for Co and Cl are from the same place, Table 3.3.2A.

TABLE I

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR [Co($C_{24}H_{36}N_4$)Cl_2]ClO_4, IN ELECTRONS (×10)

K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL
				-12	-2	373	418	11	10	343	287
**	H =	0	**	13	2	240	258	12	10	204	108
				-14	-2	352	354	0	11	550	547
2	0	1455	1711	0	3	1109	1187	-1	-11	404	406
4	0	1388	1302	-0	-3	224	259	-3	-11	290	238
6	0	964	943	1	3	844	833	5	11	243	249
8	0	383	422	-1	-3	984	1006	7	11	246	190
10	0	865	990	2	3	847	880	8	11	284	232
12	0	666	666	-2	-3	906	806	9	11	222	232
16	0	238	257	3	3	262	211	-9	-11	255	266
18	0	287	278	-3	-3	723	690	10	11	235	261
0	1	1531	1709	4	3	231	186	-0	-12	256	246
1	1	1567	1669	-4	-3	352	282	-1	-12	317	332
2	1	1120	1270	5	3	154	199	-2	-12	230	246
3	1	919	1011	-5	-3	785	807	-3	-12	200	77
4	1	885	912	6	3	396	399	4	12	290	200
6	1	155	165	-6	-3	173	188	-5	-12	215	201
8	1	476	533	7	3	342	281	6	12	261	232
9	1	648	684	8	3	560	623	8	12	349	338
10	1	271	276	-8	-3	284	301	-8	-12	196	237
11	1	487	519	9	3	245	256	10	12	301	268
12	1	286	305	-9	-3	227	240	-0	-13	338	338
13	1	268	267	10	3	514	570	1	13	240	227
0	2	490	531	-10	-3	465	469	-2	-13	203	202
1	2	697	632	-11	-3	320	314	3	13	301	257
2	2	254	249	-12	-3	392	400	7	13	237	202
3	2	2096	2082	14	3	272	122	9	13	319	347
4	2	690	661	-14	-3	235	218	-10	-13	177	204
5	2	494	768	16	3	242	221	-0	-14	182	157
7	2	128	143	17	3	218	155	-1	-14	218	260
8	2	313	267	-0	-4	663	624	-2	-14	206	188
9	2	876	875	1	4	336	351	-6	-14	185	90
10	2	329	355	-1	-4	632	584	0	15	194	203
11	2	495	520	2	4	584	614	-1	-15	224	241
12	2	302	236	-2	-4	172	210	2	15	193	170
13	2	240	290	-3	-4	359	359	-3	-15	236	238
0	3	939	1014	4	4	462	461				
1	3	286	279	-4	-4	497	471	**	H =	2	**
2	3	1298	1226	5	4	378	377				
3	3	211	214	-5	-4	438	407	0	0	107	115
4	3	152	104	6	4	322	327	1	0	1512	1494
5	3	513	461	-6	-4	240	253	2	0	1421	1573

TABLE I (*Continued*)

K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL
-7	-7	220	215					4	3	252	287	-3	-5	382	404	-5	-8	217	272	-4	-1	301	306	-6	-2	366	396	6	4	275	292	-5	-8	244	282	-0	-3	215	222	-1	-1	216	202	-7	-3	179	149
-9	-7	232	159	0	0	230	245	-6	-3	200	145	-5	-5	240	269	-3	-9	197	274	4	1	276	285	6	2	325	313	-0	-5	214	214	-2	-9	203	220	-2	-3	196	198	1	1	196	183	-2	-4	204	227
-0	-8	254	230	1	1	203	228	7	3	259	312	7	5	207	224	3	9	185	164	-5	-1	350	380	9	2	210	248	-2	-5	208	240	-4	-10	191	206	5	3	200	176	-2	-1	196	133	-4	-4	265	268
-2	-8	276	304	-3	-1	192	213	0	4	212	179	-1	-6	289	272	-6	-9	185	143	6	1	278	336	-1	-3	251	190	-3	-5	290	294					-1	-4	216	164	4	1	260	215	-7	-4	196	192
-7	-8	193	93	5	1	224	276	-2	-4	233	261	-2	-6	254	207	-4	-10	182	128	-7	-1	272	300	-2	-3	244	168	-4	-5	229	220	**	H = 13	**		5	4	196	113	-5	-1	189	174	-5	-6	194	174
-0	-9	247	259	0	2	284	259	2	4	210	224	2	6	239	151	-2	-11	194	215	7	1	318	319	-3	-3	221	122	4	5	256	195					-1	-5	248	232	5	1	207	146				
0	9	201	163	3	2	324	297	-3	-4	224	272	6	6	241	220					8	1	305	317	-4	-3	300	287	6	5	288	259	7	0	239	230	4	5	207	207	7	1	198	161	**	H = 15	**	
-3	-9	212	233	5	2	297	270	3	4	335	336	-0	-7	301	312	**	H = 12	**		-11	-1	232	163	-5	-3	278	194	-4	-6	269	300	0	1	254	206	-0	-6	224	144	-1	-2	252	265				
-10	-9	225	196	8	2	207	234	-4	-4	261	182	0	7	207	92					-2	-2	235	236	5	3	297	289	-7	-6	194	103	-1	-1	308	302	1	7	192	118	2	2	190	184	-3	-1	182	123
-0	-10	222	211	9	2	231	106	-5	-4	219	190	-2	-7	246	259	3	0	271	295	3	2	215	204	-6	-3	315	322	-3	-7	235	244	-5	-1	251	254	-3	-9	168	125	-3	-2	234	232	-0	-2	177	86
-0	-11	232	229	10	2	224	145	6	4	271	286	3	7	243	181	5	0	278	298	-4	-2	439	462	7	3	284	330	5	7	184	185	6	1	223	257					3	2	202	180	-3	-4	197	211
-2	-11	183	128	13	2	201	148	8	4	220	281	6	7	196	162	6	0	249	270	4	2	245	192	-1	-4	311	326	-6	-7	190	225	1	2	216	165	**	H = 14	**		-5	-2	193	238				
				-2	-3	421	448	1	5	241	241	8	7	210	210	7	0	274	322	-5	-2	251	322	-3	-4	318	337	-1	-8	208	237	-5	-2	223	227					1	3	193	133				
**	H = 11	**		-4	-3	216	251	-2	-5	245	239	3	8	213	227	-3	-1	236	331	5	2	226	215	-5	-4	245	196	-3	-8	285	272	6	2	217	181	-0	-1	281	283	-5	-3	197	174				

TABLE II

FINAL ATOMIC PARAMETERS FOR $[Co(C_{24}H_{36}N_4)Cl_2]ClO_4$[a]

Atomic Coordinates

Atom	x	y	z	B	Atom	x	y	z	B
Co(1)	0.1082(3)	0.2376(origin)	0.1251(3)	-	C(13)	0.2900(20)	0.0986(19)	-0.1774(21)	4.33(75)
Co(2)	0.6162(3)	0.2386(4)	0.1633(3)	-	C(14)	0.3140(18)	0.0389(16)	-0.0969(20)	3.42(68)
Cl(1)	-0.0102(5)	0.1403(5)	0.1326(5)	-	C(15)	0.3236(17)	0.0762(16)	0.0179(18)	2.75(62)
Cl(2)	0.2251(6)	0.3364(5)	0.1242(6)	-	C(16)	0.0667(18)	0.2998(17)	-0.0763(19)	3.41(67)
Cl(3)	0.7485(5)	0.2997(5)	0.1041(5)	-	C(17)	-0.0265(18)	0.3223(16)	-0.0200(19)	2.79(60)
Cl(4)	0.4689(5)	0.1839(5)	0.2134(5)	-	C(18)	-0.0579(16)	0.4136(15)	-0.0434(17)	2.18(58)
Cl(5)	0.9108(6)	0.4134(6)	0.3364(6)	-	C(19)	-0.1122(22)	0.4175(19)	-0.1545(22)	4.42(79)
Cl(6)	0.4447(8)	0.3799(7)	-0.1025(7)	-	C(20)	-0.0664(18)	0.4373(16)	-0.2422(21)	3.02(66)
O (1)	0.9106(13)	0.4510(12)	0.2366(15)	5.35(52)	C(21)	-0.1136(20)	0.4341(17)	-0.3409(21)	4.08(71)
O (2)	0.9728(17)	0.4475(16)	0.4096(19)	9.06(78)	C(22)	-0.2191(22)	0.4192(18)	-0.3484(22)	4.72(76)
O (3)	0.8045(19)	0.4177(17)	0.3660(19)	9.80(85)	C(23)	-0.2699(20)	0.4078(18)	-0.2675(22)	4.20(72)
O (4)	0.9357(18)	0.3287(17)	0.3241(18)	9.12(74)	C(24)	-0.2216(21)	0.4042(18)	-0.1653(21)	4.01(75)
O (5)	0.3909(23)	0.4307(22)	-0.1605(26)	14.09(123)	C(25)	0.7059(17)	0.1030(15)	0.0799(18)	2.54(59)
O (6)	0.5050(27)	0.3335(24)	-0.1770(28)	17.21(132)	C(26)	0.6037(19)	0.1189(18)	0.0085(20)	4.12(72)
O (7)	0.4999(27)	0.4246(23)	-0.0280(28)	16.16(133)	C(27)	0.6136(21)	0.0961(18)	-0.1115(21)	4.53(73)
O (8)	0.4028(27)	0.3141(26)	-0.0636(27)	16.82(137)	C(28)	0.7091(20)	0.1123(17)	-0.1500(19)	3.72(71)
N (1)	0.1226(13)	0.2369(14)	0.2773(13)	2.87(45)	C(29)	0.7328(23)	0.1947(20)	-0.2040(22)	5.19(78)
N (2)	0.0981(14)	0.2230(11)	-0.0230(13)	2.48(50)	C(30)	0.8285(24)	0.2058(20)	-0.2433(22)	5.40(86)
N (3)	0.2245(14)	0.1651(12)	0.1312(16)	2.80(54)	C(31)	0.9001(20)	0.1540(19)	-0.2380(21)	3.90(74)
N (4)	0.0045(13)	0.3200(12)	0.0929(14)	2.36(49)	C(32)	0.8822(23)	0.0779(21)	-0.1880(22)	5.26(90)
N (5)	0.6763(13)	0.2610(12)	0.3022(13)	2.78(48)	C(33)	0.7913(22)	0.0576(18)	-0.1423(21)	4.26(80)
N (6)	0.5486(15)	0.3449(13)	0.1680(15)	3.58(55)	C(34)	0.5984(17)	0.3150(15)	0.3570(17)	2.28(57)
N (7)	0.5814(13)	0.2062(12)	0.0182(13)	2.30(49)	C(35)	0.5654(19)	0.3765(17)	0.2800(20)	3.70(69)
N (8)	0.6776(13)	0.1302(12)	0.1803(14)	2.11(44)	C(36)	0.4617(19)	0.4209(17)	0.3004(20)	3.82(70)
C (1)	0.2241(17)	0.1162(16)	0.2316(19)	3.18(65)	C(37)	0.4760(20)	0.4521(19)	0.4056(24)	3.72(76)
C (2)	0.2097(20)	0.1857(18)	0.3150(20)	3.96(71)	C(38)	0.5103(27)	0.5277(27)	0.4134(31)	8.55(121)
C (3)	0.1769(17)	0.1366(17)	0.4181(19)	3.25(64)	C(39)	0.5196(26)	0.5607(23)	0.5349(29)	7.45(108)
C (4)	0.1803(24)	0.1997(19)	0.5046(21)	4.35(75)	C(40)	0.5027(24)	0.5057(24)	0.6103(25)	6.24(90)
C (5)	0.2709(23)	0.2222(20)	0.5593(24)	6.26(89)	C(41)	0.4522(27)	0.4380(26)	0.5762(32)	8.30(117)
C (6)	0.2695(26)	0.2865(21)	0.6441(25)	6.29(92)	C(42)	0.4410(20)	0.4129(18)	0.4854(25)	4.44(79)
C (7)	0.1891(28)	0.3226(22)	0.6577(24)	6.36(94)	C(43)	0.7534(17)	0.1357(15)	0.2696(18)	2.24(56)
C (8)	0.0978(29)	0.3019(26)	0.6106(29)	8.91(116)	C(44)	0.7873(19)	0.0500(17)	0.3065(20)	3.75(75)
C (9)	0.0918(22)	0.2340(21)	0.5225(21)	5.52(78)	C(45)	0.8580(20)	0.0611(17)	0.4178(22)	3.99(72)
C(10)	0.2155(16)	0.1198(15)	0.0299(17)	2.12(55)	C(46)	0.8170(20)	0.1042(18)	0.4919(21)	4.24(75)
C(11)	0.1930(16)	0.1818(15)	-0.0530(16)	1.81(54)	C(47)	0.7813(20)	0.1965(18)	0.4515(20)	3.98(70)
C(12)	0.1775(17)	0.1418(16)	-0.1546(18)	2.99(64)	C(48)	0.7059(17)	0.1826(15)	0.3541(17)	2.15(56)

Anisotropic thermal parameters[b]

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co(1)	0.00405(30)	0.00193(19)	0.00454(33)	0.00072(26)	0.00069(24)	-0.00071(28)
Co(2)	0.00417(31)	0.00289(20)	0.00373(31)	-0.00075(28)	0.00042(24)	0.00049(29)
Cl(1)	0.00428(55)	0.00367(43)	0.00486(61)	0.00011(41)	0.00112(44)	0.00112(41)
Cl(2)	0.00659(66)	0.00237(40)	0.00833(74)	-0.00057(42)	0.00076(53)	-0.00055(44)
Cl(3)	0.00427(56)	0.00398(43)	0.00735(66)	-0.00095(41)	0.00040(48)	-0.00091(45)
Cl(4)	0.00330(55)	0.00439(42)	0.00615(63)	-0.00044(40)	-0.00027(47)	0.00026(44)
Cl(5)	0.00571(71)	0.00597(57)	0.00679(75)	-0.00084(50)	-0.00040(57)	-0.00115(53)
Cl(6)	0.01148(96)	0.00621(62)	0.00768(86)	-0.00027(69)	-0.00065(75)	0.00118(64)

[a] Numbers in parentheses are estimated standard deviations from the least-squares refinement; X 10^2 for isotropic thermal parameters, X 10^5 for anisotropic thermal parameters, and X 10^4 for all other parameters.

[b] The form of the thermal ellipsoid is $\exp[-(h^2\beta_{11}+k^2\beta_{22}+\ell^2\beta_{33}+2hk\beta_{12}+2h\ell\beta_{13}+2k\ell\beta_{23})]$ where β_{ij} are related to the mean-square amplitude tensors by the expression, e.g., $\beta_{12}=2\pi^2U_{12}a^*b^*$.

light atoms to final R_1, R_2 values of 0.096, 0.098.[6] A difference map calculated from the final data set showed some light-atom thermal anisotropy as expected but otherwise indicated a reasonably complete refinement. Undoubtedly the somewhat high value for the final R factor is a result of omitting anisotropic thermal corrections for the light atoms, but the question of molecular conformation in the coordination sphere appeared to be adequately answered, and the refinement was terminated. The choice of enantiomer was subsequently verified with $\bar{h}\bar{k}\bar{l}$ data as discussed in a later section. Table I compares observed and calculated structure factors for the final calculation, and Table II lists the final atomic parameters.

ORD and CD Data.—Optical rotatory dispersion and circular dichroism measurements were made using 0.1-mm and 1.0-cm cells at 25 ± 2° on a Cary 60 ORD-CD instrument, and the absorption spectrum was measured on a Beckman DK-2A spectrometer. Spectral grade methanol was used as the solvent in both cases.

Discussion of the Structure

Bonding.—Figure 2 gives a stereoview of the asymmetric unit. The two independent molecules have identical configurations and chelate ring conformations, but the conformations of the remaining portions of the molecules are different as a result of crystal packing forces. Bond distances are given in Table III. Co–N

TABLE III

BOND DISTANCES AND SOME BOND ANGLES IN $[Co(C_{24}H_{36}N_4)Cl_2]ClO_4$

Molecule I				Molecule II			
Co(1)-N(1)	1.970(18)Å	Cl(5)-O(1)	1.44(2)Å	Co(2)-N(5)	1.947(17)Å	Cl(6)-O(5)	1.30(3)Å
Co(1)-N(2)	1.933(18)	Cl(5)-O(2)	1.33(2)	Co(2)-N(6)	1.988(21)	Cl(6)-O(6)	1.52(4)
Co(1)-N(3)	1.953(20)	Cl(5)-O(3)	1.49(2)	Co(2)-N(7)	1.978(18)	Cl(6)-O(7)	1.38(4)
Co(1)-N(4)	1.963(19)	Cl(5)-O(4)	1.46(3)	Co(2)-N(8)	1.986(19)	Cl(6)-O(8)	1.35(4)
Co(1)-Cl(1)	2.264(8)			Co(2)-Cl(3)	2.218(8)		
Co(1)-Cl(2)	2.261(8)			Co(2)-Cl(4)	2.296(8)		
C(1)-N(3)	1.54(3)	C(16)-N(2)	1.50(3)	C(25)-N(8)	1.46(3)	C(34)-N(5)	1.58(3)
C(2)-N(1)	1.48(3)	C(17)-N(4)	1.49(3)	C(26)-N(7)	1.49(3)	C(35)-N(6)	1.54(3)
C(1)-C(2)	1.61(4)	C(16)-C(17)	1.53(3)	C(25)-C(26)	1.60(3)	C(34)-C(35)	1.47(3)
C(2)-C(3)	1.66(3)	C(17)-C(18)	1.60(3)	C(26)-C(27)	1.62(3)	C(35)-C(36)	1.60(3)
C(3)-C(4)	1.54(3)	C(18)-C(19)	1.56(3)	C(27)-C(28)	1.42(3)	C(36)-C(37)	1.46(3)
C(4)-C(5)	1.39(3)	C(19)-C(20)	1.37(3)	C(28)-C(29)	1.59(4)	C(37)-C(38)	1.34(4)
C(5)-C(6)	1.54(4)	C(20)-C(21)	1.38(3)	C(29)-C(30)	1.42(4)	C(38)-C(39)	1.67(4)
C(6)-C(7)	1.25(4)	C(21)-C(22)	1.41(3)	C(30)-C(31)	1.28(3)	C(39)-C(40)	1.37(4)
C(7)-C(8)	1.35(4)	C(22)-C(23)	1.31(3)	C(31)-C(32)	1.45(4)	C(40)-C(41)	1.37(4)
C(8)-C(9)	1.60(4)	C(23)-C(24)	1.42(3)	C(32)-C(33)	1.43(3)	C(41)-C(42)	1.25(4)
C(9)-C(4)	1.34(3)	C(24)-C(19)	1.46(3)	C(33)-C(28)	1.42(3)	C(42)-C(37)	1.34(3)
C(10)-N(3)	1.51(3)			C(43)-N(8)	1.47(2)		
C(11)-N(2)	1.51(2)	N(1)-Co(1)-N(4)	103.0(8)°	C(48)-N(5)	1.51(3)	N(6)-Co(2)-N(7)	107.8(8)°
		N(4)-Co(1)-N(2)	83.5(8)			N(7)-Co(2)-N(8)	85.3(8)
C(10)-C(11)	1.51(3)	N(2)-Co(1)-N(3)	87.2(8)	C(43)-C(44)	1.56(3)	N(8)-Co(2)-N(5)	86.5(8)
C(11)-C(12)	1.48(3)	N(3)-Co(1)-N(1)	86.9(8)	C(44)-C(45)	1.66(3)	N(5)-Co(2)-N(6)	87.1(8)
C(12)-C(13)	1.70(3)			C(45)-C(46)	1.35(3)		
C(13)-C(14)	1.46(3)	Cl(1)-Co(1)-Cl(2)	177.7(3)	C(46)-C(47)	1.68(4)	Cl(3)-Co(2)-Cl(4)	174.1(4)
C(14)-C(15)	1.61(3)	N(3)-Co(1)-N(4)	167.6(8)	C(47)-C(48)	1.56(3)	N(5)-Co(2)-N(7)	168.7(8)
C(15)-C(10)	1.62(3)	N(1)-Co(1)-N(2)	172.3(9)	C(48)-C(43)	1.53(3)	N(6)-Co(2)-N(8)	171.3(8)

distances average to 1.95 ± 0.02 Å in molecule I and 1.97 ± 0.02 Å in molecule II, in good agreement with the 1.95–2.00-Å range of the values recently reported for some bidentate ligands.[8-10] The Co–Cl distances average to 2.260 ± 0.008 Å, also in agreement with published values (2.22–2.49 Å[11,12]). Because of a lack of high-order reflections, the large weight of the heavy-atom contributions, and a considerable degree of anisotropy in thermal vibrations for some light atoms (see Figure 2), the accuracy of the structure with respect to the carbon, nitrogen, and oxygen is such that no significance can be attached to the fairly wide range of bond distances observed in those parts of the structure. However, it is interesting to note that bond distances in each of the four phenyl rings average to 1.41 ± 0.04, 1.39 ± 0.04, 1.43 ± 0.04, and 1.39 ± 0.04 Å and that the averages for the two cyclohexane rings are both 1.56 ± 0.03 Å.

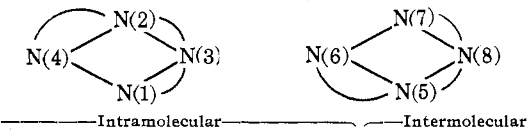
The large thermal motion in the perchlorate ions is obvious in Figure 2, and again the range of observed bond distances is large. Averaging also gives reasonable values, 1.43 ± 0.03 and 1.41 ± 0.04 Å, comparable to a recently published value of 1.43 Å.[13] Thermal parameters for the perchlorate oxygen atoms O(1)–O(4) are comparable to those for other light atoms in the molecule, and N—O nonbonded distances for these atoms range from 3.01 to 3.21 Å suggesting an ordered structure for this one of the two anions in the asymmetric unit. On the other hand, thermal parameters for O(5)–O(8) range from 14.1 to 17.2 and nonbonded distances here show a much broader spread from 2.89 to 3.48 Å, suggestive of possible disorder in this anion. The difference map, however, supports an interpretation of excessive anisotropy of motion, and both anions are treated as ordered in our model.

The geometry of the Co coordination octahedron can be seen from the bond angles given in Table III which suggest that the constraining geometry of the ligand molecule results in the opening of the N–Co–N′ angles for the terminal $-NH_2$ groups to 103.0 and 107.8° from a normal 90°. The other angles in the equatorial planes vary from 83.5 to 87.2°. The deviation of the four nitrogen atoms from their average plane is 0.10 Å in molecule I and 0.11 Å in molecule II. In both cases, to Co atoms lie very nearly in the plane, and the nitrogens alternate above and below the plane in a rotation sequence about the Cl–Co–Cl′ axis. The axial Cl–Co–Cl′ angles are 174.1 and 177.7° in molecules I and II, respectively. As expected, the five-membered chelate rings are puckered. Deviations of the atoms from their average planes range from 0.10 to 0.35 Å.

Nonbonded interactions (listed in Table IV) appear to play an important role in stabilizing the trans struc-

TABLE IV

NONBONDED DISTANCES IN $[Co(C_{24}H_{36}N_4)Cl_2]ClO_4$ (Å)[a]



Intramolecular				Intermolecular	
Cl(1)-N(1)	2.94	Cl(4)-N(5)	3.16	N(3)-Cl(4)	3.33
Cl(1)-N(2)	2.92	Cl(4)-N(6)	2.96	N(4)-Cl(3)	3.42
Cl(1)-N(3)	3.14	Cl(4)-N(7)	3.07		
Cl(1)-N(4)	3.05	Cl(4)-N(8)	2.97		
Cl(2)-N(1)	3.00	N(1)-N(4)	3.08	N(1)-O(4)	3.01
Cl(2)-N(2)	3.08	N(4)-N(2)	2.59	N(4)-O(1)	3.19
Cl(2)-N(3)	2.85	N(2)-N(3)	2.68	N(4)-O(4)	3.21
Cl(2)-N(4)	2.93	N(3)-N(1)	2.70		
Cl(3)-N(5)	2.89	N(6)-N(7)	3.07	N(5)-O(3)	3.18
Cl(3)-N(6)	2.94	N(7)-N(8)	2.68	N(6)-O(7)	2.89
Cl(3)-N(7)	2.86	N(8)-N(5)	2.69	N(6)-O(8)	3.48
Cl(3)-N(8)	3.16	N(5)-N(6)	2.71	N(7)-O(6)	3.39
				N(7)-O(8)	3.08
				N(8)-O(5)	3.46

[a] Errors are of the order of ±0.05 Å.

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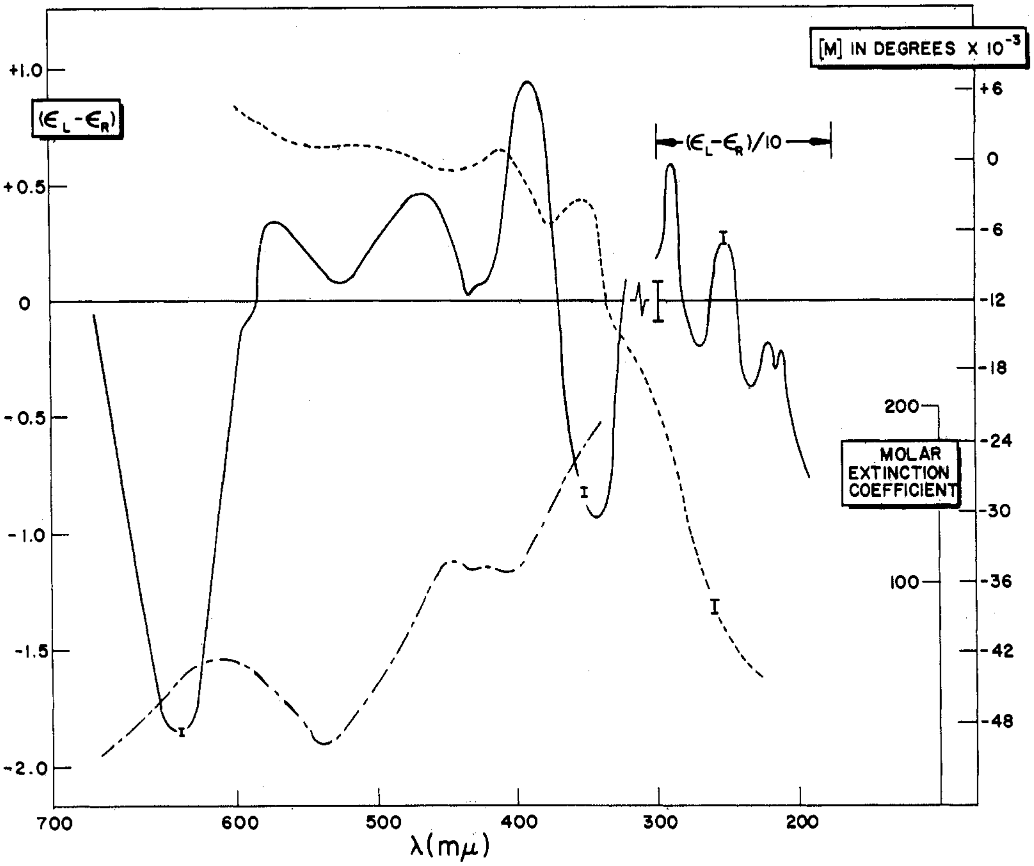

Figure 3.—Absorption (— - —), CD (—), and ORD (----) spectra of $(+)_{589}$-*trans*-$((-)_{589}$-N,N'-bis((*S*)-2-amino-3-phenylpropyl)-*trans*-(*R*)-1,2-cyclohexanediamine-δλδ)dichlorocobalt(III) perchlorate in methanol (0.0123 g/10 ml, 25 ± 2°).

ture. The N(1)–N(4) and N(6)–N(7) distances reflect the distortion of the coordination octahedra in being considerably longer than the other N–N approaches in each octahedron. The N–Cl intramolecular distances are interesting in that there is one largest value in each set of four corresponding to the nitrogen which has its hydrogen pointing away from that chlorine. The deviation of the Cl–Co–Cl′ axis from a straight line may result from weak N–H ⋯ Cl attractions, involving the three amino hydrogens on one side of the equatorial plane and the 90° rotation about the Cl–Co–Cl′ axis of the three on the other side. These N—Cl distances range from 2.85 to 3.16 Å and are, of course, a secondary result of the Co–Cl bonding but may contribute to the stability of the structure.

The 2.89-Å approach between N(6) and O(7) is in the range of distances considered to represent N–H ⋯ O hydrogen bonding, but the excessive thermal vibration observed in the O(7) perchlorate ion results in large errors for interatomic distance calculations and no such significance can be supported in this case.

Finally, it is interesting to note that the perchlorate ions pack to approach the open sides of the coordinated Co cations (see Figure 2).

Absolute Configuration.—Table V presents the anomalous dispersion data which confirm the absolute configuration of the complex as $(+)_{589}$-*trans*-$((-)_{589}$-N,N'-bis((*S*)-2-amino-3-phenylpropyl) - *trans* - (*R*) - 1,2-cyclohexanediamine-δλδ)dichlorocobalt(III) perchlorate.[14] This nomenclature (*vide infra*) combines recent conventions.[15] Our result confirms, by a direct method, the *R* configuration assigned to (+)-*trans*-cyclohexane-1,2-diamine on the basis of optical rotatory dispersion curve comparison.[16]

TABLE V

COMPARISON OF BIJVOET PAIRS FOR ABSOLUTE CONFIGURATION OF $[Co(C_{24}H_{36}N_4)Cl_2]ClO_4$

hkl	$F_o(hkl)/F_o(\bar{h}\bar{k}\bar{l})$	$F_c(hkl)/F_c(\bar{h}\bar{k}\bar{l})$	*hkl*	$F_o(hkl)/F_o(\bar{h}\bar{k}\bar{l})$	$F_c(hkl)/F_c(\bar{h}\bar{k}\bar{l})$
040	0.86	0.86	222	1.29	1.38
052	1.31	1.36	$\bar{2}22$	1.27	1.35
023	0.85	0.87	$\bar{2}13$	0.40	0.59
063	0.34	0.49	233	1.35	1.42
024	1.21	1.28	254	1.42	2.19
064	1.59	1.91	$\bar{2}54$	1.50	1.71
055	0.64	0.82	$\bar{4}11$	1.84	2.19
$\bar{1}29$	1.79	1.78	$\bar{4}12$	0.60	0.53
210	0.90	0.87	$\bar{4}44$	0.63	0.70
250	1.53	1.50	$\bar{4}15$	0.67	0.71
221	0.24	0.42	$\bar{6}25$	1.63	1.64
231	0.80	0.78			

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(14) The rotation of the ligand was measured on a solution of the tetrahydrochloride salt in H_2O.

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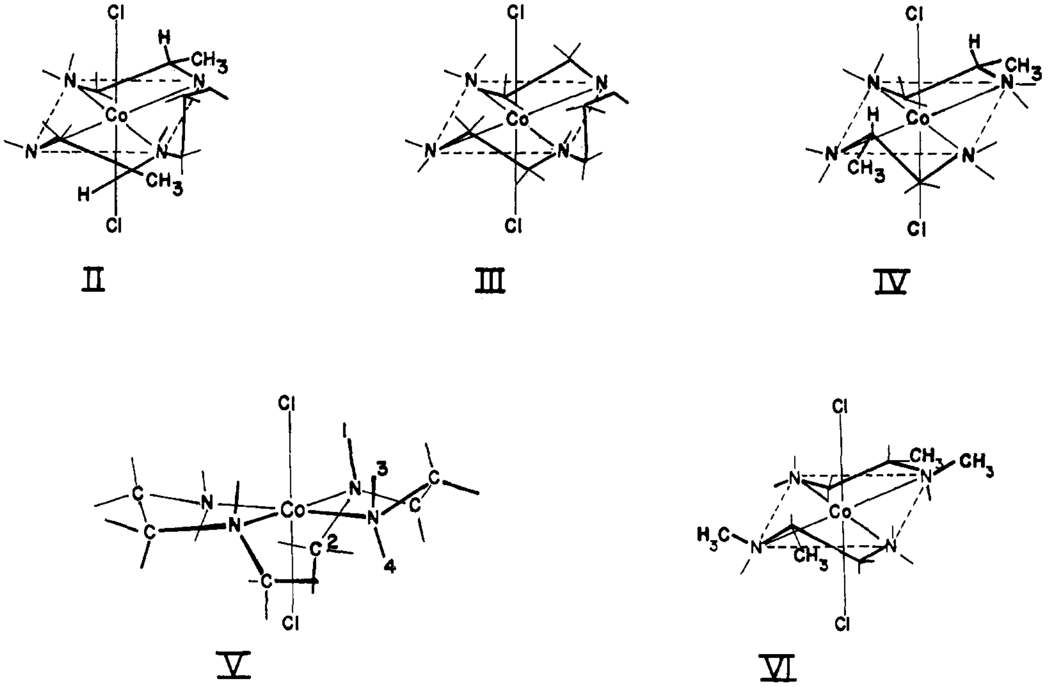
(16) Abbreviations of nomenclature used in this paper are (a) (*S*,*S*)-α,α′-$(CH_3)_2$trien for (*S*,*S*)-2,9-diamino-4,7-diazadecane, (b) (*S*)-3,8-$(CH_3)_2$-trien for (*S*,*S*)-1,8-diamino-2,7-dimethyl-3,6-diazaoctane, (c) trien for 1,8-diamino-3,6-diazaoctane (or triethylenetetramine), (d) (*S*)-pn for (*S*)-1,2-diaminopropane (or (*S*)-propylenediamine), (e) Meen for 1-amino-3-azabutane, and (f) N_1-Mepn for 1-amino-2-methyl-3-azabutane.



II III IV

V VI

Figure 4.—Structural formulas for complexes II–VI.

Discussion of the Circular Dichroism

ORD, CD, and absorption spectra for I are shown in Figure 3. The fine structure in the ultraviolet region of the curve (obtained using the 0.1-mm cell) is of considerable interest. The uncertainty of the base line in this region is large, but the absolute magnitudes of the peaks are independent of this, and the small, sharp, negative band at 214 mμ is reproducible. Consecutive runs give curves which are displaced vertically from each other due to the limitation of the instrument under these difficult experimental conditions, and this uncertainty in the base line is indicated in the figure.

The five compounds shown in Figure 4 have CD spectra similar to that for I, as seen in the comparison in Figure 5. The compounds are[16] $(+)_{589}$-*trans*-Co((*S*)-3,8-$(CH_3)_2$-trien-δλδ)Cl_2^+ (II),[17] $(+)_{589}$-*trans*-Co(trien-δλδ)Cl_2^+ (III),[18] $(+)_{546}$-*trans*-Co((*S*)-pn-δ)$_2$$Cl_2^+$ (IV),[18,19] $(-)_{589}$-*trans,trans*-(*R,R*)-Co(Meen-δ)$_2$$Cl_2^+$ (V),[1] and $(-)_{589}$-*trans,trans*-(*R,R*)-Co(N_1-Mepn-δ)$_2$$Cl_2^+$ (VI).[20] The reader is again referred to a later section for nomenclature. Compounds I–III have CD spectra in which peaks occur at nearly the same wavelength and differ only in magnitude. These differences cannot be ascribed to variations in configuration and conformation as is the case for the tris-diamine complexes of Co(III) and Pt(IV) ions,[21,22] since all three are identical in these respects. On the other hand, these complexes differ considerably in the distribution of other atoms outside the first coordination sphere, and it is suggested here that these differences give rise to the differences in the CD spectra. The sensitivity of the spectra to variations in structure can be demonstrated by considering structures III and V. Complex V goes to III if the methyl group at position 2 is interchanged with the hydrogen at position 3 and the two methyls then lose two protons and form a carbon–carbon bond to give trien. Thus the differences between the CD spectra for III and V can only be due to the relocation of one carbon atom in the first coordination sphere. Similar changes at a further distance from the coordinating ion can also be expected to give observable effects,[23–29] and changes in substituent groups on a ligand should produce changes in the CD spectrum as has been observed for steroids with F^- and phenyl substituents.[23]

Nomenclature

Nomenclature used in this paper is based on several recent proposals,[30,31] and a brief description follows to facilitate the recognition of equivalent structures given with earlier nomenclature. It must be pointed out, however, that deficiencies in nomenclature used previously have resulted in the presence of many ambiguities in the literature.

R and *S* are used to denote the absolute configuration of asymmetric carbon atoms or to refer to the absolute

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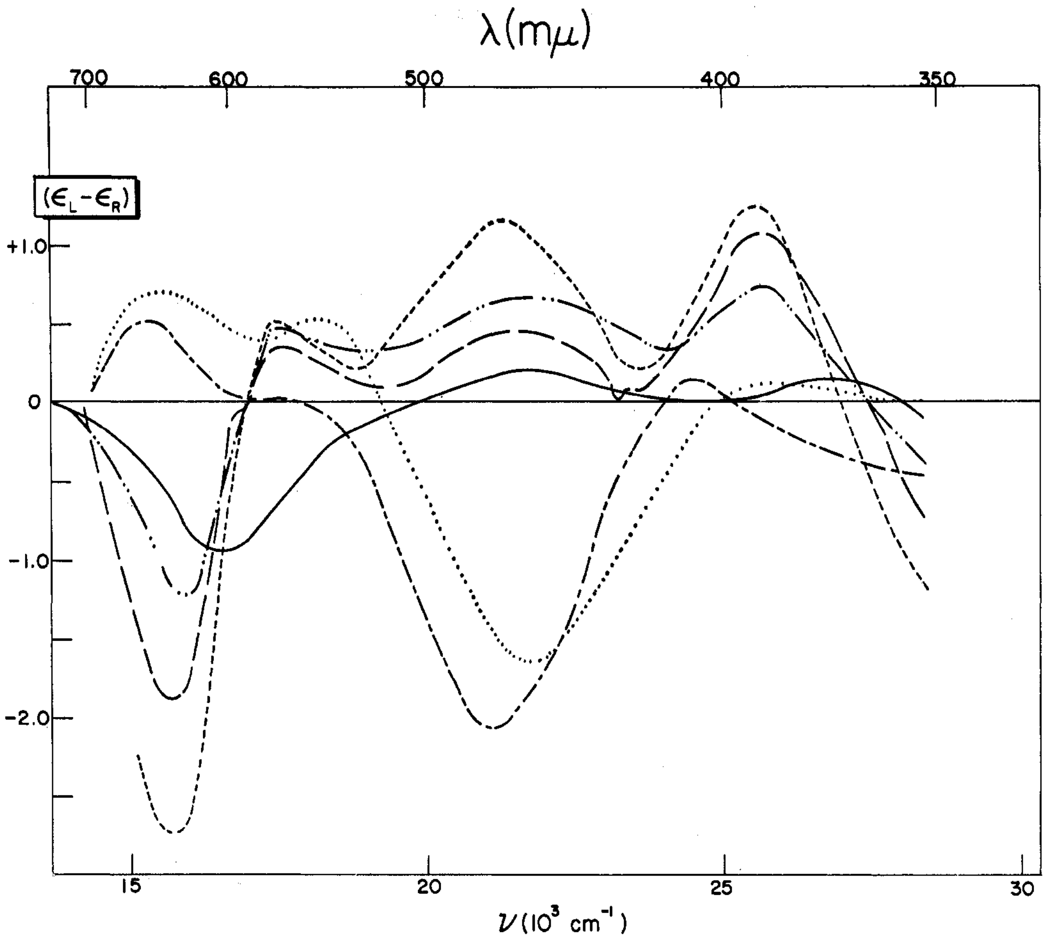

Figure 5.—A comparison of the CD spectra of II–IV with that for I: I, — —; II, ----; III, —··—; IV, ——; V, ······; VI, —-—-.

configuration of coordinated nitrogen when used preceding the bracket enclosing the ligand descriptor in a named complex. According to Mislow,[31] if the priority order of groups attached to the asymmetric atom is decreasing atomic number and for the same atomic number is decreasing isotopic mass and if the group of lowest priority is viewed *through* a triangle formed by joining the other three groups, then if the observed order of decreasing priority on the triangle is clockwise, the configuration is *R* (*rectus*), and if the order is counterclockwise, the configuration is *S* (*sinister*).

The IUPAC commission on the nomenclature of absolute configuration for six-coordinated complexes has formulated the following rule. "The line joining the two ligating atoms, AA, and the line joining the two atoms of the chelate ring adjacent to each of the ligating atoms, BB, define a helix. AA is the axis of the helix, and BB is the tangent at the common normal for the skew lines. The tangent describes a right-handed (δ) or a left-handed (λ) helix with respect to the axis and

thereby defines the conformation."

As an illustration, note that the complex $(+)_{589}$-*trans*-Co(trien-δλδ)Cl_2^+ is equivalent to $(+)_{589}$-*trans*-(*S*,*S*)-Co(trien)Cl_2^+. On the other hand, the complex written as $(-)_{589}$-*trans,trans*-(*R*,*R*)-Co(Meen)$_2Cl_2^+$ [1] has conformational ambiguity and, when written as $(-)_{589}$-*trans,trans*-Co(Meen-δ)$_2Cl_2^+$, has an ambiguity with respect to the absolute configuration of the nitrogen atoms. A precise description would be $(-)_{589}$-*trans*,-*trans*-(*R*,*R*)-Co(Meen-δ)$_2Cl_2^+$. Note also that the absolute configuration of complex III was originally described correctly[32] as $(+)_{589}$-*trans*-(*S*,*S*)-Co(trien)Cl_2^+ but was later incorrectly named[1] as $(+)_{589}$-*trans*-(*R*,*R*)-Co(trien)Cl_2^+ when referring to the same CD curve.

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(32) D. A. Buckingham, P. A. Marzilli, and A. M. Sargeson, *Inorg. Chem.*, **6**, 1032 (1967).